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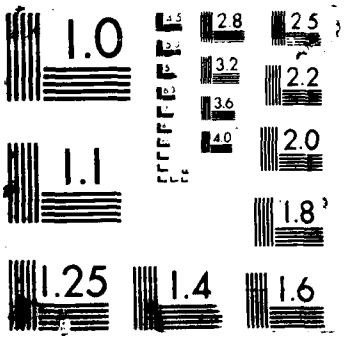
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DIFFUSION NOISE ANNEALED Na, Ag AND Pbβ"ALUMINA

by

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Abstract

Conductivity fluctuations in Pbβ"alumina arising from diffusion of the mobile ions are observed to increase linearly with annealing time at a temperature of 130°C after quenching from 550°C. Simultaneously, the conductivity as measured by Nyquist noise decreases linearly. No effect of annealing on conductivity fluctuations or conductivity is found for either Naβ"alumina or Agβ"alumina. The increase in conductivity fluctuations for Pbβ"alumina can be interpreted in terms of a decrease in effective ion density for diffusion noise.

INTRODUCTION

Several x-ray and neutron crystal structure studies[1] of the β"aluminas have presented evidence for two-dimensional ordering of the mobile ions in the conduction planes, with room temperature coherence lengths ranging from 10 to 200A°. In the case of Na"alumina, the change in coherence length with temperature accounts reasonably well for the non-Arrhenius behavior of the conductivity[2]. It has been observed that annealing heat treatment can introduce changes in site occupancies by the mobile ions and in the long-range order[3]. For example, while rapidly-cooled Pbβ"alumina has the highest room temperature conductivity of the divalent β"aluminas, slow cooling or annealing at modest temperatures (130°C) leads to decreases in conductivity of many orders of magnitude[4].

Conductivity fluctuations in the β"aluminas[5,6] are ascribed to diffusion noise of the mobile ions. The magnitude of the noise is

much greater and the temperature dependence different from that predicted by the standard expression for diffusion noise[7], and these discrepancies may be a result of correlation effects between the mobile ions. Experimentally observed diffusion noise[8] is similar for different mobile ion species, but differs quantitatively, which also could be attributable to differences in ionic correlations.

This study examines the effect of annealing heat treatments on conductivity fluctuation diffusion noise in single crystal and ceramic Na, Ag, and Pbβ"alumina. These mobile ion species are chosen because of the differences in correlations between the ions and because of the expected differences in the effect of annealing upon correlation effects. The experimental work is facilitated by the ease with which mobile ions can be exchanged in the β"alumina structure[9].

EXPERIMENTAL TECHNIQUE

Sodium β"alumina (90.4% Al_2O_3, 8.85% Na_2O, 0.75% Li_2O) ceramic specimens[10] and single crystals[11] approximately 5x5x0.5 mm^3 are converted[12] to Agβ"alumina or Pbβ"alumina by ion exchange in molten 50% $AgNO_3/NaNO_3$ at 300°C for 8 hours or by immersion in molten $PbCl_2$ at 550°C for 24 hours under a partial pressure of oxygen. Weight change of the converted samples indicates essentially complete exchange of silver or lead ions for the mobile sodium ions. The corners of the samples are sealed into the sides of four plastic test tubes containing appropriate liquid electrode materials to provide diagonally opposing corner current contacts and transverse noise contacts. This configuration reduces the possible influence of contact current noise on conductivity fluctuations observed at the transverse contacts[13].

Low noise, ohmic contacts are provided by 0.5M NaI propylene carbonate solution, 5M $AgNO_3$ aqueous solution, or saturated aqueous $Pb(NO_3)$ in the four test tubes. In each case, contact noise is negligible after aging for several hours. Transverse noise voltages

are measured with a PAR 113 preamplifier and a digital FFT PC analyzer[14].

Before mounting, each sample is heated in a Helium atmosphere at 550°C and quenched by surrounding it with a water-cooled metal sleeve. Some samples are heated in air and quenched on a metal block to increase the cooling rate. The samples are then annealed in air at 130°C for various times up to 30 hours. Periodically, the Nyquist noise and diffusion noise levels are determined after pouring the appropriate electrode solution into the test tubes. Fresh electrode solution is used after each annealing interval.

EXPERIMENTAL RESULTS

Typical experimental noise spectra for Naβ"alumina and Agβ"alumina are shown in Figures 1 and 2. These data are in good agreement with previous results[5] in that the conductivity determined from the Nyquist noise level agrees with literature values, and the -3/2 slope of the conductivity fluctuation spectra is characteristic of diffusion noise. In neither case is there a difference in either Nyquist noise or diffusion noise resulting from annealing.

The results are quite different for Pbβ"alumina, Figures 3 and 4. Here both the Nyquist noise level (hence the resistivity) and the diffusion noise level are observed to increase linearly with annealing time. The Nyquist noise level before annealing is considerably greater than that calculated from the sample dimensions and literature values of the conductivity. Single crystals do not exhibit this discrepancy[6], which may mean that the lead ions are not uniformly distributed in the ceramic samples.

DISCUSSION

In one dimension, the standard expression for the noise voltage spectral density, S(V,f,T), of conductivity fluctuations due to diffusion is[7]

$$\frac{S(V,f,T)}{V^2} = 2\,\frac{\langle \Delta N^2 \rangle}{N^2}\left(\frac{2D}{L^2}\right)^{1/2} \quad [1-\exp(-r)(\cos r+\sin r)]\;\omega^{-3/2}$$

$$r = L(\omega/2D)^{1/2} \qquad (1)$$

Where $\langle \Delta N^2 \rangle$ is the total variance and N the average number of diffusing ions, D is the diffusion constant, L is the sample length, and V is the voltage across the sample. At frequencies well above the characteristic frequency, $2D/L^2$ (given by r=1), the expression reduces to

$$\frac{S(V,f,T)}{V^2} = \frac{2}{N}\left(\frac{2D}{L^2}\right)^{1/2}\;\omega^{-3/2} \qquad (2)$$

Where Poisson statistics $\langle \Delta N^2 \rangle = N$, are assumed. Equation (2) is an example of the so-called universal -3/2 power law characteristic of diffusion[15].

Experimental results in Figures 1, 2, and 3 are in agreement with equations (1) and (2), except that the observed noise voltages are very much greater and the temperature dependence[1,8] is different than predicted, if N is determined by the known density of mobile ions, about 10^{21} ions/cm^3. The standard expression for diffusion noise is developed assuming independent diffusing entities[15], and the observed disagreement is taken as evidence for correlations between or ordering of the mobile ions.

On this basis, annealing heat treatments that increase the mobile ion order are expected to influence both the Nyquist noise level, through a decrease in conductivity, and the diffusion noise level, as observed. The absence of either effect in Na and Agβ"alumina means that annealing does not lead to such ordering in these materials.

Equation (2) may be used to calculate an effective ion density from the experimental data. It is assumed that the measured change in conductivity results from a decrease in the diffusion constant with annealing time and the diffusion constant is determined using the Einstein relation,

$$D = (kT/e)\mu = kT/ne^2)\sigma \qquad (3)$$

where k is Boltzman's constant, T is the temperature, e is the electronic charge, μ is the ionic mobility and σ is the conductivity. The calculated effective ion density decreases with annealing, as shown in Figure 5 for two different Pbβ"alumina ceramic samples.

The decrease in effective ion density seems to be conceptually in keeping with ordering of the mobile ions. A more quantitative understanding awaits a treatment of diffusion noise that accounts for correlations between the mobile ions. In addition, it is important to repeat the experiments with Pbβ"alumina single crystals to eliminate the possible disturbing influence of grain boundaries.

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* On leave from Shanghai Institute of Ceramics, Chinese Academy of Science.

REFERENCES

1. J. P. Boilot, G. Collin, Ph. Colomban and R. Combes, Phys. Rev., B22, 5912 (1980); K. G. Frase, J. O. Thomas, and G. C. Farrington, Solid State Ionics, 9&10, 307 (1983).
2. G. Collin, J. P. Boilot, Ph. Colomban, and R. Combes, Phys. Rev., B34, 5838 (1986); Phys. Rev., B34, 5850 (1986).
3. M. A. Saltzberg, P. K. Davis, and G. C. Farrington, Mat. Res. Bull., 21, 1533 (1986).
4. P. K. Davis, private communication.
5. J. J. Brophy and S. W. Smith, J. Appl. Phys., 58, 351 (1985); "Noise in Physical Systems and 1/f Noise - 1985", North-Holland, New York (1986), p. 243; J. Appl. Phys., 61, 581 (1987).
6. J. J. Brophy and J. J. Carroll, "Noise in Physical Systems - 1987", C. M. Van Vliet (ed), World Scientific, Singapore, (1987), p. 305.
7. K. M. Van Vliet and J. R. Fassett, "Fluctuation Phenomena in Solids", Academic Press, New York, (1965), p. 268.
8. J. J. Brophy, ONR Technical Note No. 16, to be published.
9. J. L. Briant and G. C. Farrington, J. Solid St. Chem., 33, 385 (1980); G. C. Farrington and B. Dunn, Solid State Ionics, 7, 267 (1982).
10. Ceramatec, Inc., Salt Lake City, Utah, 84115.
11. Airtron, Inc., Morris Plains, N.J., 07950
12. R. Seevers, J. DeNuzzio, and G. C. Farrington, J. Solid State Chem., 50, 256 (1983).
13. T. G. M. Kleinpenning, J. Appl. Phys., 48, 2946 (1977).
14. S. W. Smith, Rev. Sci. Instrum., 56, 159 (1985).
15. M. Lax and P. Mengert, J. Phys. Chem. Solids, 14, 248 (1960).

FIGURE CAPTIONS

Figure 1. Nyquist noise and diffusion noise spectra of a Naβ"alumina single crystal after quenching from 550°C and after annealing for 6 hours at 130°C.

Figure 2. Nyquist noise and diffusion noise spectra of a Agβ"alumina ceramic sample after quenching from 550°C and after annealing at 130°C for 30 hours.

Figure 3. Nyquist noise and diffusion noise spectra of a Pbβ"alumina ceramic sample after quenching from 550°C and after annealing at 130°C for 12.5 hours.

Figure 4. Increase in diffusion noise and Nyquist noise with annealing time for two Pbβ"alumina ceramic samples.

Figure 5. Decrease in effective ion density with annealing time for the same samples as in Figure 4.

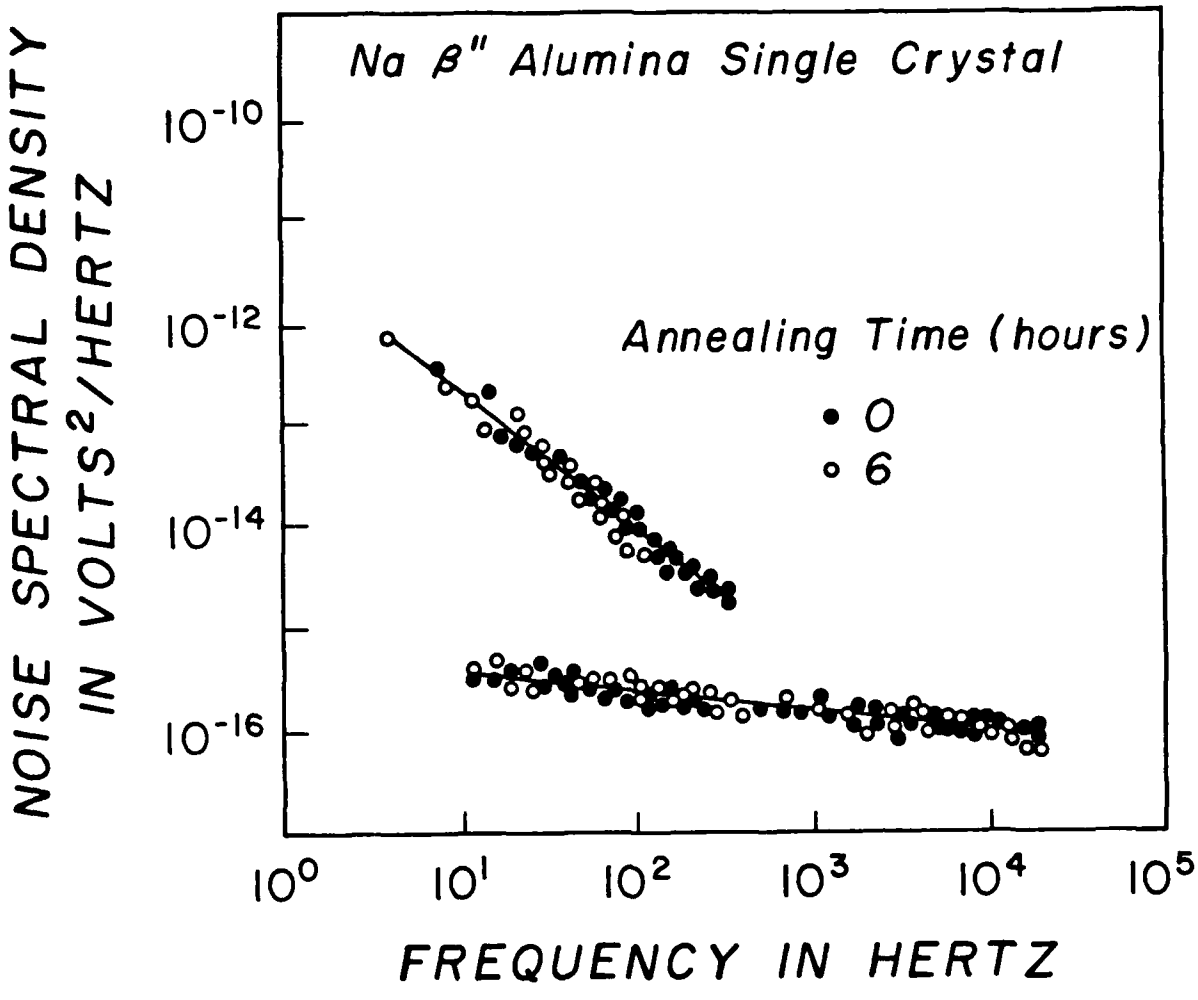
Na β" Alumina Single Crystal
Annealing Time (hours)
• 0
∘ 6
NOISE SPECTRAL DENSITY IN VOLTS²/HERTZ
10⁻¹⁰
10⁻¹²
10⁻¹⁴
10⁻¹⁶
10⁰
10¹
10²
10³
10⁴
10⁵
FREQUENCY IN HERTZ

Figure 1

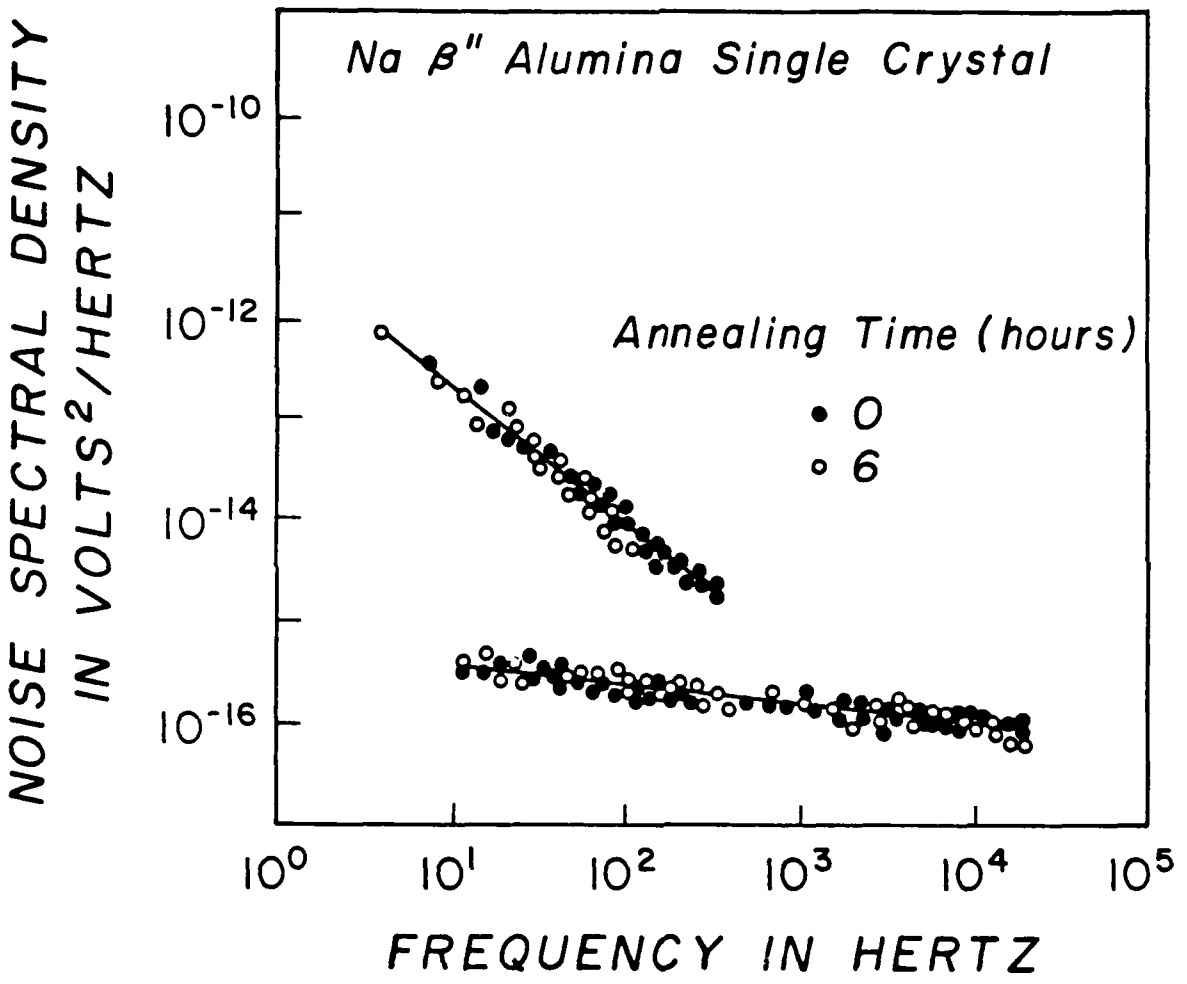
Na β" Alumina Single Crystal
Annealing Time (hours)
• 0
∘ 6
NOISE SPECTRAL DENSITY IN VOLTS²/HERTZ
10⁻¹⁰
10⁻¹²
10⁻¹⁴
10⁻¹⁶
10⁰
10¹
10²
10³
10⁴
10⁵
FREQUENCY IN HERTZ

Figure 2

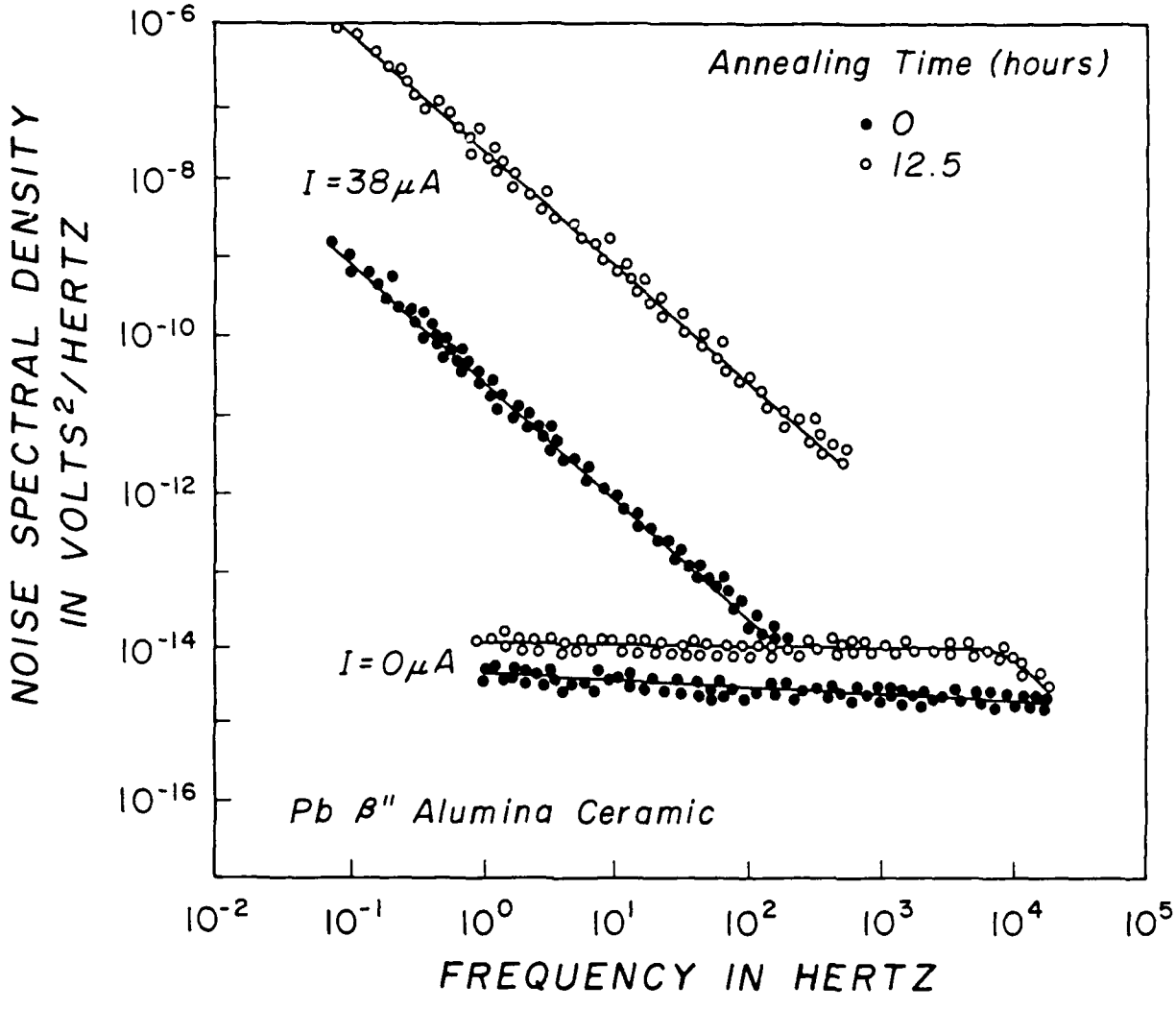
NOISE SPECTRAL DENSITY
IN VOLTS²/HERTZ
10⁻⁶
10⁻⁸
10⁻¹⁰
10⁻¹²
10⁻¹⁴
10⁻¹⁶
Annealing Time (hours)
• 0
∘ 12.5
I = 38μA
I = 0μA
Pb β" Alumina Ceramic
10⁻²
10⁻¹
10⁰
10¹
10²
10³
10⁴
10⁵
FREQUENCY IN HERTZ

Figure 3

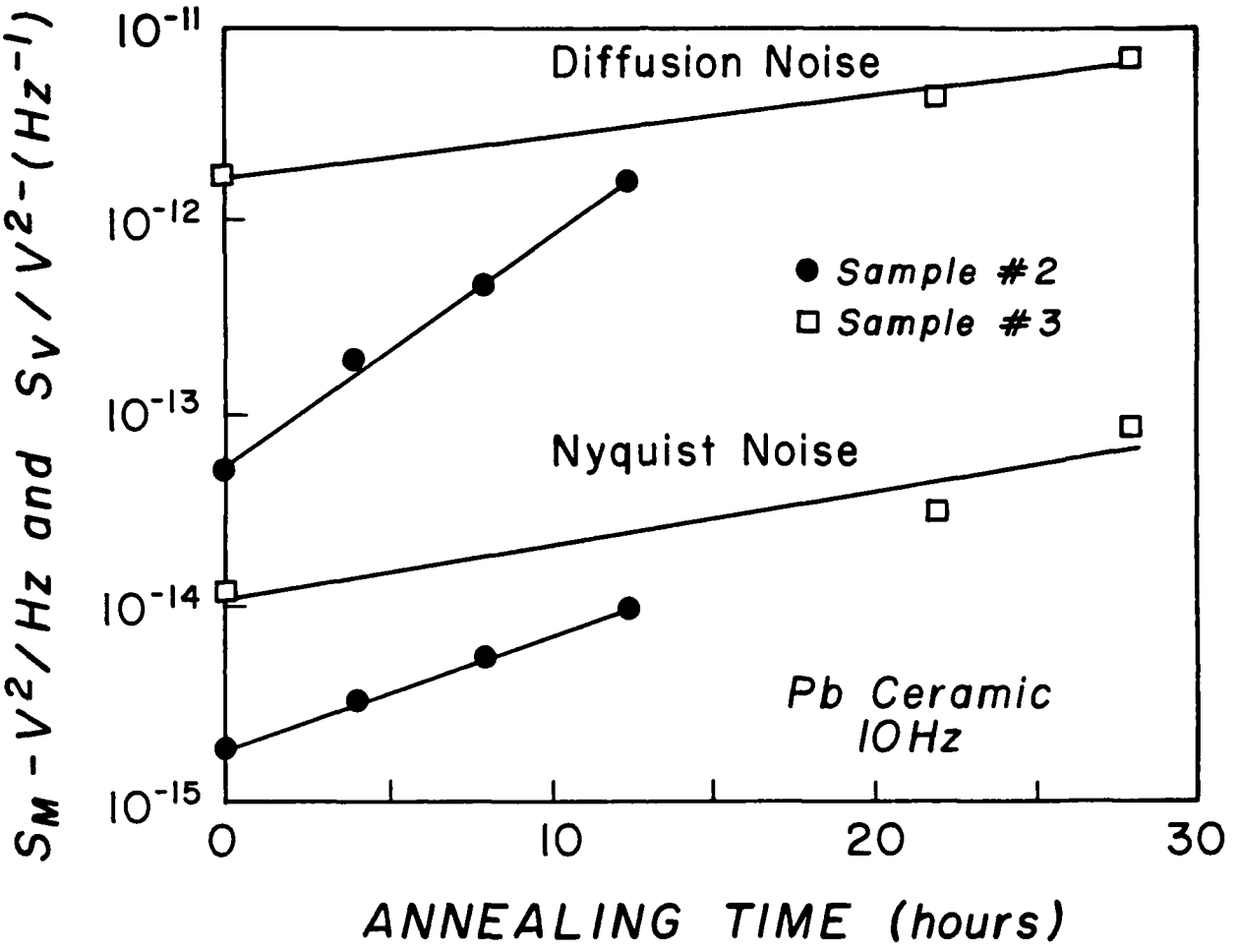
10^{-11}
10^{-12}
10^{-13}
10^{-14}
10^{-15}
Diffusion Noise
Sample #2
Sample #3
Nyquist Noise
Pb Ceramic
10Hz
0
10
20
30
$S_M - V^2/Hz$ and $Sv/V^2-(Hz^{-1})$
ANNEALING TIME (hours)

Figure 4

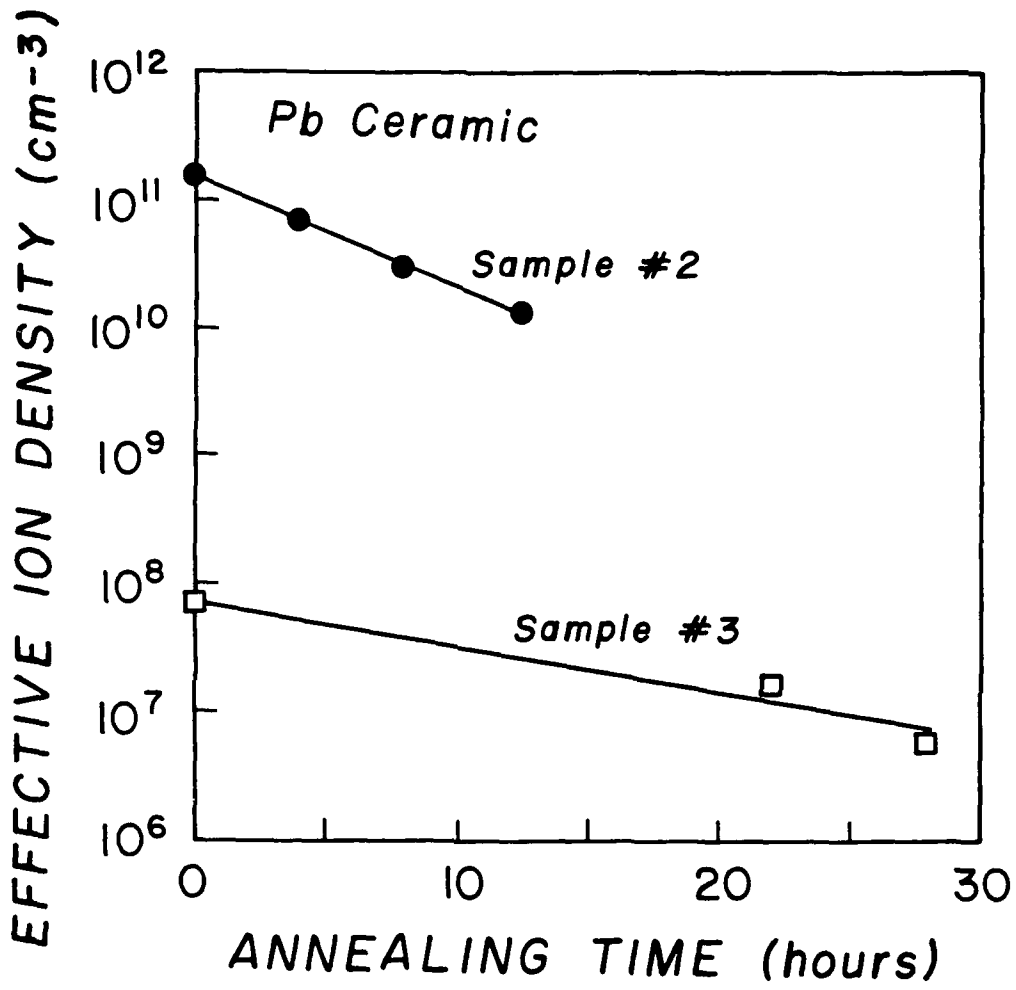
Pb Ceramic
Sample #2
Sample #3
EFFECTIVE ION DENSITY (cm-3)
10^{12}
10^{11}
10^{10}
10^{9}
10^{8}
10^{7}
10^{6}
0
10
20
30
ANNEALING TIME (hours)

Figure 5

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